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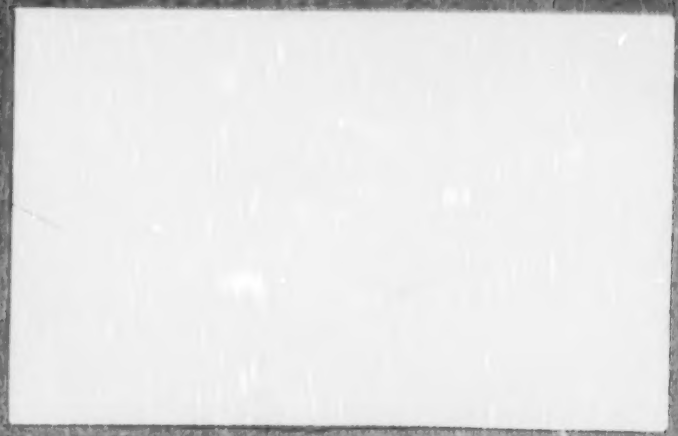

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DEVELOPMENT OF A METHOD FOR THE DETERMINATION OF CARBON AND HYDROGEN IN SOLID WASTE

A Division of Research and Development
Open-File Report (RS-03-68-17)

written by
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U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
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1970

ABSTRACT

Characterization of solid wastes materials is necessary in the planing, designing, operation, and evaluation of refuse processing and disposal systems and facilities. A literature survey of existing methods revealed that a generally new macroanalytical technique would have to be developed for the determination of carbon in solid wastes materials. With this method the chemist must be able to analyze a one to two gram sample of dry, generally uniform, solid waste substance for its total carbon content, which may exist in various forms and may range in concentration from approximately 10 to 60 percent.

An investigation into the basic types of carbon methods revealed that the dry combustion-purification-gravimetric approach, which also yields the hydrogen content of samples, is the most promising. This report is an account of the development of such a carbon-hydrogen method.

The newly developed method permits the analyst to determine precisely and accurately the carbon and hydrogen contents of all types of solid waste materials. With this new method solid wastes samples can have a carbon content of 0.5% to 83.0% and a hydrogen content of 0.01% to 7.80%; however, all substances must be thoroughly dried and generally uniform before being analyzed. Normally between one to two grams (not less than one gram) samples were used in each determination, although as much as ten grams can be employed. Since this method is specifically designed for application to the

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determination of macro amounts of carbon and hydrogen in solid wastes samples, sample portions of solid wastes material less than one gram should not be used for analysis.

TABLE OF CONTENTS

		Page
	Abstract	iii
I.	Introduction	1
II.	Approach	2
III.	Results	4
IV.	Conclusions	15
V.	References	16
VI.	Appendix	18
	A. Figures and Tables	
	B. Cost	
	C. Sample Preparation Procedures	

I. Introduction

The carbon and hydrogen contents of various solid wastes materials are important to some volume reduction processes used to dispose of wastes. In the case of incineration, the efficiency of operation of an incinerator can be measured by material balance techniques, in which carbon and hydrogen analyses are essential. In view of the fact that incinerator residue or compost may be used for land filling, and the stability of these solid wastes products is a function of their carbon and hydrogen contents, the carbon and hydrogen analyses must be performed.

Conventional carbon-hydrogen methods either required an extremely homogeneous sample because of the small amount of material (usually 50 mg) analyzed or a low carbon content sample (less than 6%) which contains no impurities which affect the carbon-hydrogen analyses. Solid wastes samples are two heterogeneous and contain too many interferences for these conventional methods.

The newly developed carbon-hydrogen method described herein overcomes the problems of analyzing solid wastes materials with conventional methods. However, the precision and accuracy of the new carbon-hydrogen method, as with most solid wastes methods, is greatly affected by sample preparation techniques. Therefore, the sample preparation procedures used during the development of the carbon-hydrogen method are discussed in this report (Appendix).

II. Approach

The six basic means of analyzing samples for their carbon contents are: (1) Gravimetric, [1,2,3,4,5,6] in which the sample is combusted and the carbon dioxide evolved is absorbed and weighed; (2) Volumetric [7,8] in which the carbon dioxide evolved during sample combustion is collected in a solution which is then titrated to an end point with a standard acid solution; (3) percent Ash Relationship [9] where the sample is muffled at 600 C and carbon content is calculated using a previously established relationship between the ash and carbon content; (4) Alkalimetric [10] where a combination of acids, catalysts, and heating techniques convert all the carbon in the sample to carbon dioxide and the carbon content is calculated from the loss in sample weight; (5) Manometric [11] in which carbon dioxide, released from an acid-sample reaction, is measured by the volume it displaces in a calibrated manometer; (6) Oxygen-Flask [12] in which the sample is ignited electrically in a specially designed flask which contains a carbon dioxide absorbent.

The gravimetric system which also reveals hydrogen content of samples, appeared to be the most promising means of analyzing solid waste samples. The volumetric methods involve absorption solutions which may not be capable of absorbing large amounts of carbon dioxide emitted from solid wastes materials. The percent ash relationship technique, although sometimes used for compost samples, has not shown a consistant relationship between the percent ash and the carbon content of samples. The alkalimetric system

relies upon an acid-catalyst-heat combination which cannot handle such heterogeneous solid wastes samples. The manometric method relies upon (1) acids which cannot react with all the carbon in solid wastes materials and (2) an absorbing column which is not selective for carbon dioxide only. The oxygen-flask procedure cannot completely combust all solid wastes substances and is hazardous to the analyst.

Having selected the gravimetric approach, the next step was to determine what chemicals and equipment were necessary. According to the literature of conventional methods, the gaseous impurities which affect the results in the gravimetric method are fluoro-compounds, oxides of sulfur, oxides of nitrogen, and halogens. Since solid wastes materials usually contain all these interfering impurities, the carbon-hydrogen train (Figures 1. and 2.) was constructed to remove these substances.

After several modifications (already incorporated in Figures 1. and 2.), the carbon and hydrogen contents of pure sucrose could be analyzed accurately and precisely. The applicability of this modified method in analyzing each type of solid wastes materials was established by : (1) varing the sample weights to insure complete combustion; (2) adding excess interfering impurities to insure their removal; (3) adding various forms of carbon to insure the complete recovery of all types of carbon.

After the method was proven satisfactory for analyzing each type of solid wastes materials the precision of the method was established for each type of material.

III. Results

The literature survey involved a review of the last ten years of chemical abstracts, various books, and personal communications.

Since a furnace which fulfilled the requirements of the gravimetric method was unavailable, a construction and purchase contract was awarded to the Lindberg Company whose technical staff then altered the design and function of their Hevi-Duty, Organic Carbon, Multiple Unit, Tube Type, Electric Furnace Model 123-T* to meet our specifications.

The gravimetric method requirements placed upon the furnace were: (1) the furnace must have a 2" bore which could handle a ceramic tube, 1 1/2 inch O. D. and 30 inches long; (2) the furnace must have three sections, 8, 12, 4 inches, respectively. The temperatures of the three sections must be 900, 800, and 200 degrees centigrade, respectively and be individually controlled.

When the carbon-hydrogen train was put into operation, the 30-inch ceramic tube proved to be too short and caused the rubber stopper to burn slightly. A 38-inch Vycor tube was found superior, especially since the action taking place in the tube could be observed and the tube could be easily cleaned. If a Vycor tube is not available, a ceramic tube, longer than 30 inches, could be used. After a 25 day-investigation of 12 variables (Table 1) the modified gravimetric method was successfully employed to analyze NBS grade sucrose.

*Product (or manufacturer) identification shown in this report does not imply endorsement by the United States Public Health Service.

The effect of each of the 12 variables was evaluated independently. The first investigation involved a comparison of the applicability of a glass baffle versus a ceramic baffle. The glass baffle is shorter and produces a better baffling effect; however, it is more costly and needs modification. Although the ceramic baffle breaks more easily, its cost is so much less than the glass baffle that the breakage cost is not significant. The less efficient baffling aspect of the ceramic baffle proved to have no effect upon the sample analyses. The decision was therefore made to use the ceramic baffle rather than the glass type.

The change in baffle types did affect the sample insertion procedure (the next variable listed in Table 1). The original sample insertion procedure was to insert the sample into a cold combustion zone, heat to 900 C, then cool to remove the sample. This insertion procedure required much time and strained the heating elements of the furnace. A sample inserter was devised which allowed the analyst to insert the sample slowly into an already hot combustion zone. If this insertion is too fast the exothermic combustion reaction produces too much pressure and causes the stopper, baffle, and sample inserter to be shot out of the combustion tube. Inserting the sample container one inch per five minutes prevents a too violent reaction. Although the ceramic baffle causes the sample's initial position to be closer to the combustion zone,the insertion procedure works satisfactory with either the ceramic or glass baffle.

Keeping the combustion zone at a constant temperature affords longer life to the heating elements and allows greater control over the tempera-

ture. This greater temperature control permitted the combustion temperature to be raised to 950±50 C, closer to the maximum furnace temperature of 1010 C. Since the decomposition temperature of calcium carbonate is 898 C, the temperature increase to 950 C assured the conversion of all the calcium carbonate present in a sample to carbon dioxide.

The gaseous mixture from the sample combustion first goes through a special packing mixture of platinized asbestos, asbestos, and aluminum oxide (Figure 3). The platinum assures the conversion of any methyl groups to carbon dioxide. The aluminum oxide removes any fluoro-compounds which would be collected in the carbon dioxide adsorbing material and hence affect the carbon result. Mixing these ingredients prevents the aluminum oxide from caking and inhibiting the gas flow.

Next, the mixture of gases diffuses through lead chromate, 12-20 mesh or powder which has been fused at 820 C for one hour to prevent caking. The lead chromate removes oxides of sulfur by oxidizing any sulfur dioxide to sulfur trioxide and, finally, to the non-volatile lead sulfate. Since the lead chromate functions best at about 600 C, the lead chromate is located so that it is heated by the cooler end zones of the 12-inch furnace which is maintained in the center at 800 C. A one-inch air gap between the 8-inch and 12-inch furnaces allows for a temperature gradient and does not allow the moisture from the combustion to condense in this area which has an outside tube temperature of 160 C midway between the furnaces. Between the lead chromate is copper oxide which converts any carbon monoxide to

carbon dioxide and functions best at about 800 C. Several endeavors were performed before the right combination of positions and quantities of the lead chromate and copper oxide was accomplished.

After leaving the second lead chromate section, the gaseous mixture passes through silver wool (wool was found easier to pack than wire). The silver wool's purpose is to remove the halogens.

Lead dioxide follows the silver wool and removes oxides of nitrogen. The lead dioxide made some modifications in the procedure necessary. Firstly, the hygroscopic-lead dioxide is affected by the moisture in the system and if a blank is analyzed with this ingredient in the tube, the following sample analyses will be incorrect. Thus, the blank analyses must be performed using an unpacked combustion tube. Secondly, the problem with the lead dioxide is the low temperature (usually 190 C) at which it performs. When the lead dioxide is maintained at 190 C with the 4 inch-furnace, water vapors from the combustion of the sample condense in this area of the tube. Employing a temperature of 200 C, wrapping the reduced end of the combustion tube with aluminum foil, and using an oxygen flow of 250cc. per minute prevent the formation of liquid water in this area of the combustion tube. Again an air gap is made between furnaces to allow a temperature gradient; but, the gap does not allow moisture to condense in the tube since the outside tube temperature is 175 C midway between the furnaces. This air gap is one-half inch and is between the

12-inch and 4-inch furnaces.

The oxygen gas flow rates tried were in the range of: 50 to 100 cc./min.; to 200 to 300 cc./min.; and 350 to 400 cc./min. A gas flow rate of 250 cc/min. is the minimum rate that can be used. A slower flow rate does not enable the system to be flushed sufficiently in the one hour-analysis-time and allows a back flow of gases when the sample ignition occurs.

The minimum sample combustion period, starting with the placement of a sample container in the combustion tube and ending with the removal of the absorption bulbs, is 60 minutes when an oxygen flow rate of 250 cc./min. is employed. Other combustion periods of 30, 45, 75, and 90 minutes were evaluated and found undesirable.

The carrier gas used in this method is oxygen, 99.5 percent pure and prepared from liquid air. Before the oxygen goes into the combustion tube it is purified by passing it through: (1) concentrated sulfuric acid, which removes water and sulfur dioxide; (2) magnesium perchlorate, which removes any remaining water; (3) Ascarite, which removes carbon dioxide; (4) activated alumina, which removes water created by the reaction between Ascarite and carbon dioxide. A valve, located before the concentrated sulfuric acid, prevents the back flow of acid when the oxygen is turned off. A flowmeter is located after the purification system for regulating the oxygen flow at 250 cc./min. A glass stopcock, T-bore, follows the flowmeter and allows the oxygen to be diverted if too much pressure builds up during sample ignition. If this glass stopcock is closed while the train is not being used

for one-half hour or more, the need for continuous reconditioning of the combustion tube is eliminated.

A freshly packed combustion tube contains too much moisture and must be dried by flowing the dry-purified-oxygen through the tube at 250 cc./min. for at least two hours. After which, the train is checked by analyzing pure sucrose until accurate results are obtained. Once the train has been utilized, the combustion tube needs reconditioning only if it has been idle for more than one day. The reconditioning of a used tube involves analyzing a standard until the results are accurate; usually only one or two analyses are needed. Because the lead dioxide is affected by the moisture in the system, a standard, similar in nature to the material being analyzed, must precede the analyses of each type of solid wastes material.

The density of a sample is the only factor that determines the type of boat or container utilized to hold the sample. The types of containers tried included ceramic and low carbon nickel boats of various sizes, usually 3 to 6 inches long. These boats were made mainly for carbon analysis; however, all boats and their lids are ignited at 950 C for one hour in a muffle furnace and stored in a desiccator until needed. Tests showed that making fluffy samples into pellets in order to fit the 1-2 gram samples into small boats yields low results.

The types of absorption bulbs used to collect the carbon dioxide and the water were: Nesbitt, Miller, and Stetser-Norton. The efficiency of these bulbs did not differ. However, the Nesbitt type is preferred because it is easier to clean after the absorption of the carbon dioxide and

when the glass stopper is turned both the inlet and exit openings are closed to the atmosphere. The cheaper Stetser-Norton bulbs performed satisfactorily for the water collection. Glass fittings of these bulbs and all other fittings were lubricated with a nonreactive Kel-F #90 grease. All absorption bulbs must be loosely packed to enable the free flow of gases.

Since magnesium perchlorate is more efficient at absorbing water than many materials, such as, Drierite or silica gel, it was the only substance tried for the water absorption and presented no problems. Only two absorption bulbs were ever needed for the collection of all the water vapors.

Although Ascarite (8-20 mesh) can be used to collect the carbon dioxide gas, Indicarb (6-10 mesh) is preferred because it has 50 percent greater capacity for collecting carbon dioxide than Ascarite and has less tendency to cake which stops the flow of gases. Activated alumina should be placed on top of the Indicarb to collect the water which results from the reaction of the carbon dioxide and sodium hydroxide. Several absorption bulbs, never less than two, were needed for collecting all the carbon dioxide.

For absolute insurance of complete combustion, an accelerator must be employed with each sample. The two types of combustion aids tried were Combax, iron chips, and Combustion-Accelerator, granular tin metal. Either accelerator may be used, but the cheaper iron chips are preferred. The position of the accelerator does produce a difference in the final results. The best technique is to sparsly sprinkle a small amount of accelerator

over the weighed sample and, using a spatula, throughly mix the accelerator throughout the sample.

To determine if the gases are flowing through the train satisfactorily and if any carbon dioxide is escaping in the exit gas, a gas washer containing 150 ml of carbon dioxide detecting solution is employed at the exit end of the train. The presence of high carbon content and/or interferences in a sample can reduce the flow of the exit gas almost to zero. As a safety precaution, if the exit gas flow stops completely for one or two minutes the glass stopock must be turned to divert the oxygen flow from entering the combustion tube to the room air. The analyst must observe this exit gas flow rate periodically to assure the system is operating correctly. At times, the carbon dioxide absorbent cakes and stops the gas flow; however, an explosion will not occur if the inhibition of gas flow is noticed in time and the absorption bulb is removed. If the sample is highly combustible, two absorption bulbs may not collect all of the carbon dioxide. If carbon dioxide does escape the last absorption bulb it will be detected in the exit gas washer solution. Rosolic acid solution, which turns red with addition of bicarbonates plus carbon dioxide or faintly yellow with carbon dioxide only, was tried as a carbon dioxide detecting solution. A more satisfactory solution is 150 ml of barium hydroxide-thymolphthalein solution. A good preparational procedure for this detecting solution is 150 ml of barium hydroxide solution (12.0 grams to one liter) plus

0.5 ml of thymolphthalein solution (1.0 gram to 100 ml of ethanol). This detection solution turns from blue to blue-white or white upon the absorption of carbon dioxide.

With one goal being a carbon-hydrogen method that would analyze compounds containing various forms of carbon within one actual percent of the true value, the accuracy of this newly developed method was established as satisfactory (Table 2). For these tests, naphthol and urea were selected to represent hydrocarbons. Graphite was employed as elemental form of carbon and calcium carbonate as an inorganic form.

The applicability of this new carbon-hydrogen method in analyzing solid wastes material was investigated (Table 3). Because the possibility existed that sand particles may retain part of the carbon during combustion, ordinary sand and sodium silicate along with various forms of carbon were added to each type of solid wastes material. These additives produced no affects upon the method's capability of analyzing solid wastes materials (Table 3).

Experiments proved the combustion tube packing removes even large excesses of interferring substances from every type of solid wastes sample (Table 3).

As a precaution against the samples collecting moisture before being weighed for analyses and after the initial drying in sample preparation procedures [13] (Appendix), all samples must be redried no more than a few days before the analyses are performed. The procedures found for this redrying are that those samples which were originally dried at 70 C must be redried at 70 C for four hours and those samples originally dried at 105 C must be redried at 105 C for one hour. Studies showed that after

initial drying, the age of the sample, the type of storage, or the redrying procedures have no effect upon the carbon and hydrogen results. After the redrying procedures had been performed all samples were kept in tightly closed containers and in a desiccator until the analyses. Weighed samples with containers and lids were kept in a desiccator until each was inserted into the combustion tube.

The precision of the new method was determined by analyzing, in triplicate, a number of solid waste samples of various types. The pooled standard deviation of the observations for each type of solid wastes was calculated using Olivetti Underwood Programma 101. The calculations revealed that, in the analysis of each type of wastes, the duplicate and triplicate determinations were equally precise (Table 4). A calculation of the residual error between the 2-replicate and 3-replicate analysis was performed by a statistician [14] using the observed contents of 20 compost samples, and confirmed our calculations.

With this macro method the analyst normally uses a one to two-gram sample, but he is not restricted to this amount. Compost samples up to ten grams have been analyzed with no difficulty; however, the extra sample weights add little to the precision of this method.

The great effect upon the precision is the preparation procedures of the heterogeneous solid waste material. This was demonstrated when a sample, prepared in the unual manner (Appendix), was analyzed before and after additional preparation. The sample used for this study was the "fines" fraction of an incinerator residue. This sample fraction, after the usual prep-

arations, was visibly nonuniform which caused poor precision in the carbon and hydrogen analyses (Table 5). This sample was further separated into three portions, each of which was analyzed for carbon and hydrogen. The carbon and hydrogen average values of these three portions add up to less than the average values of the original sample, which indicates that, not only is the precision of the analyses of the original sample bad; it is impossible to obtain a uniformly mixed sample and hence an accurate average carbon or hydrogen value with three observations (Table 5).

One of the three portions of the above residue (fines) sample could not be ground with the Wiley Mill, or pulverized with the Iler Pulverizer. This portion was studied so that we could understand the reason why it could not be ground or pulverized. A biologist [15] performed a microscopic examination of the sample and found the following: wood charcoal and sawdust-65% or more; magnetic iron; hematite; copper; quartz; calcite; asphalt; wood resins; coal ash; soft metal of some type-chrome or aluminum identified. A research chemist [16] performed an emission spectrographic analysis on a nitric-hydrochloric acid solution of the sample portion, which unfortunately only partly dissolved in this acid medium. His analysis of the solution revealed that the major constituents were zinc, iron, aluminum, copper, and lead. Also present, in smaller concentrations, were boron, manganese, nickel, and barium. Cadmium, arsenic, molybdenum, beryllium, silver, cobalt, chromium, vanadium, and strontium were all either absent

or below the detection limits.

Exactly why this sample portion could not be ground or pulverized is still not clear. Perhaps just this particular combination of ingredients caused the problem. This sample protion was the only material our laboratory has received that could not successfully be prepared for analyses using the Wiley Mill or Iler Pulverizer. Although the problem is unresolved, the likelihood of this situation reoccurring is rare.

IV. Conclusions

A macro-carbon-hydrogen method is now available which can analyze 1 to 2 gram samples of solid waste materials. These materials can contain almost any impurity of any concentration and these carbon-hydrogen analyses are not affected. This method can accurately analyze samples whose carbon contents are between 0.46 and 83.31 percents or whose hydrogen contents are between 0.01 and 7.80 percents.

Before the carbon-hydrogen analyses can be performed the samples must be throughly dry. To ensure good precision the particle size of the sample must be less than 2 mm or pass through a #60 sieve, then thoroughly mixed before analyzing.

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VI. Appendix

A. Figures and Tables

B. Cost

C. Sample Preparation Procedures

FIGURE 1. The carbon-hydrogen train

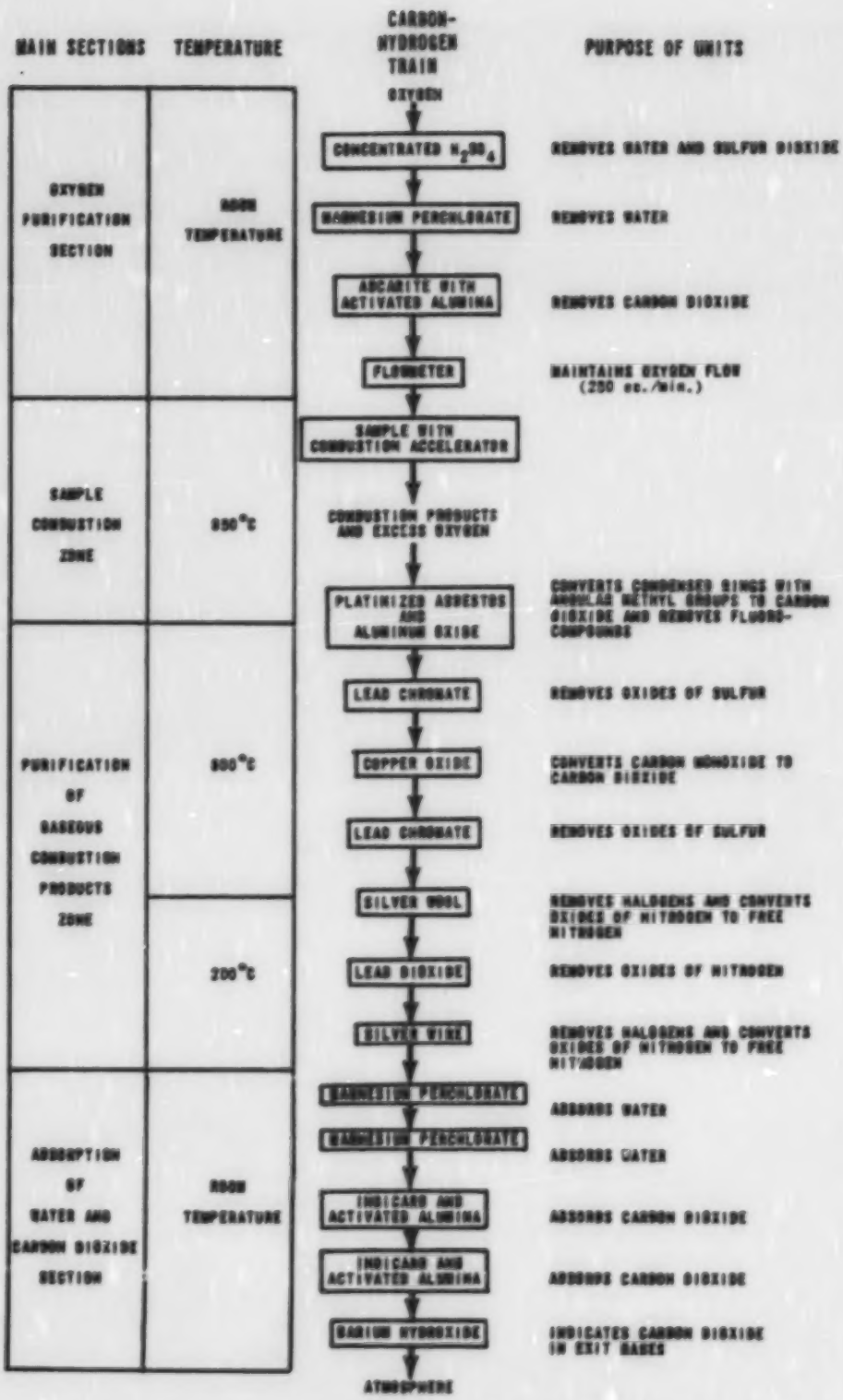

FIGURE 2. General outline of carbon-hydrogen train.

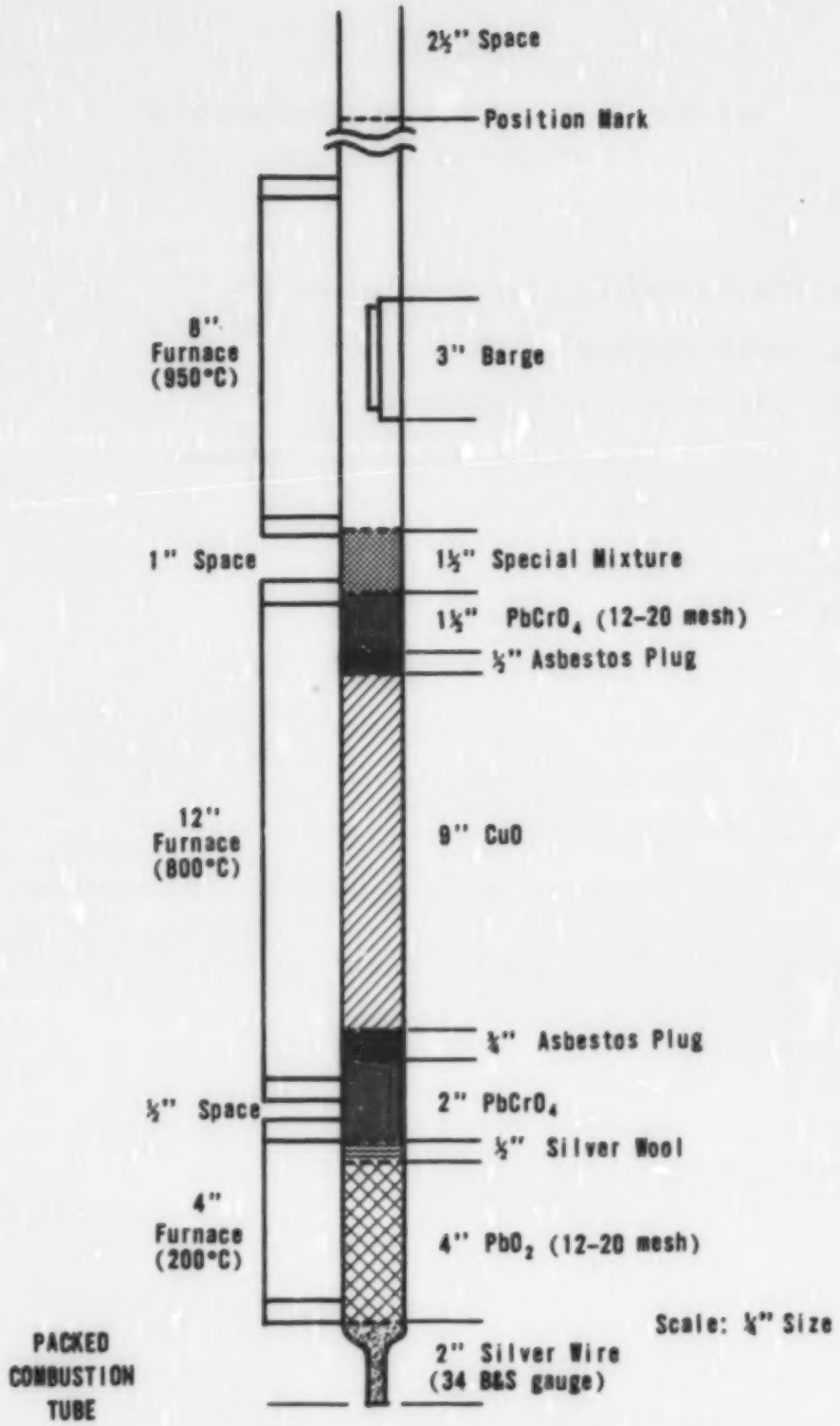

FIGURE 3. Packed combustion tube

TABLE 1

VARIABLES INVESTIGATED IN THE ESTABLISHMENT OF
THE CARBON-HYDROGEN METHOD

1. Type of baffles, glass versus ceramic
2. Sample insertion procedure
3. Temperature of each furnace
4. Amount and position of each packing ingredient
5. Position of each furnace
6. Flow rate of oxygen
7. Time for each sample analysis
8. Conditioning procedure for packed combustion tube
9. Type of boats or sample containers
10. Type of absorption bulbs
11. Position and type of combustion aids
12. Kind of solution for detecting carbon dioxide in exit gas

TABLE 2

PERCENT ACCURACY OF CARBON AND HYDROGEN DETERMINATIONS OF STANDARD COMPOUNDS

Compound	No. of determ.	%Element calcd.		%Element found.		%Recovery.	
		C	H	C	H	C	H
Sucorse, NBS	6	42.10	6.48	42.07	6.39	99.93	98.61
Sucrose, ACS	6	42.09	6.48	42.02	6.39	99.83	98.61
1-Naphthol, ACS	3	83.31	5.59	82.72	5.86	99.29	104.83
Urea	3	19.99	6.71	19.38	6.66	96.95	99.25
Calcium Carbonate	3	11.97	-	12.04	-	100.58	-
Graphite[a]	3	83.28	-	84.01	-	100.88	-

[a]Since graphite is not pure, it was ignited in air at 1150 C to determine the percent ash impurities.

TABLE 3

EFFECT OF ADDED INTERFERING SUBSTANCES ON PERCENT CARBON CONCENTRATION IN SOLID WASTES[a]

Sample Type	Additive	Percent additive in Analyzed Samples	Percent Carbon Concentration		
			Observed[b]	Changed	
				Possible	Observed
Compost-A	----	----	23.96	----	----
Compost-A	Fluorine (F^-)	0.29 - 0.58	24.10	3.53 to	0.14
	Sulfur (S^{+6})	0.52 - 1.06		7.19	
	Chlorine (Cl^-)	0.69 - 1.41			
	Nitrogen (N^{+3})	0.46 - 0.94			
Compost-B	----	----	26.35	----	----
Compost-B	Carbon as:		26.09[c]	12.91 to	0.26
	Sucrose	6.57 - 21.96		26.52	
	Urea	0.76 - 1.19			
	Graphite[d]	2.96 - 5.02			
	Calcium - Carbonate	0.41 - 0.79			
Raw Garbage-A	----	----	43.51	----	----
Raw Garbage-A	Fluorine (F^-)	0.82 - 0.89	43.38	10.09 to	0.13
	Sulfur (S^{+6})	1.48 - 1.61		10.99	
	Chlorine (Cl^-)	1.98 - 2.16			
	Nitrogen (N^{+3})	1.32 - 1.44			
Raw Garbage-A	Carbon as:		43.46	12.01 to	0.05
	Sucrose	2.68 - 8.83		19.95	
	Urea	1.85 - 2.38			
	Graphite	5.95 - 7.33			
	Calcium-Carbonate	0.70 - 1.41			

TABLE 3 CONT'D

Sample Type	Additive	Percent additive in Analyzed Samples	Percent Carbon Concentration		
			Observed[b]	Changed	
				Possible	Observed
Residue-A (Fines)[e]	——	——	9.94	——	——
Residue-A (Fines)	Fluorine (F^-)	0.57 - 0.60	9.67	7.00 to 7.38	0.17
	Sulfur (S^{+6})	1.02 - 1.08			
	Chlorine (Cl^-)	1.37 - 1.44			
	Nitrogen (N^{+3})	0.92 - 0.97			
Residue-A (Fines)	Carbon as:				
	Sucrose	4.78 - 5.79	9.91	13.38 to 15.88	0.03
	Urea	1.33 - 1.70			
	Graphite	4.60 - 8.64			
	Calcium-Carbonate	0.61 - 1.29			
Residue-B (Organics)[f]	——	——	30.52	——	——
Residue-B (Organics)	Fluorine (F^-)	0.71 - 0.82	30.37	8.78 to 10.15	0.15
	Sulfur (S^{+6})	1.29 - 1.49			
	Chloride (Cl^-)	1.72 - 1.99			
	Nitrogen (N^{+3})	1.15 - 1.33			
Residue-B (Organics)	Carbon as:				
	Sucrose	3.35 - 7.99	30.40	12.17 to 16.72	0.12
	Urea	1.31 - 2.23			
	Graphite	5.73 - 7.98			
	Calcium-Carbonate	0.65 - 1.00			

TABLE 3 CONT'D

Sample Type	Additive	Percent additive in Analyzed Samples	Percent Carbon Concentration		
			Observed[b]	Changed	
				Possible	Observed
Fly Ash-A	———	———	11.39	———	———
Fly Ash-A	Fluorine (F^-)	0.55 - 0.87	11.40	6.77 to 10.69	0.01
	Sulfur (S^{+6})	0.99 - 1.57			
	Chlorine (Cl^-)	1.32 - 2.09			
	Nitrogen (N^{+3})	0.89 - 1.40			
Fly Ash - A	Carbon as:				
	Sucrose	3.61 - 6.24	11.29	14.69 to 16.77	0.10
	Urea	1.53 - 2.09			
	Graphite	7.79 - 9.42			
	Calcium - Carbonate	0.85 - 0.92			

[a]Hydrogen values are not shown because no extra precautions were taken against the complex samples collecting moisture during weighing.

[b]Values represent the average of at least three individual determinations.

[c]Concentration of carbon in solid wastes material after substracting theoretical amounts of carbon added.

[d]Repeat of "a" of Table 1.

[e]"Fines" are materials remaining after most of the readily combustible substances have been removed by manual sorting.

[f]"Organics" are mostly the readily combustible materials.

TABLE 4

STANDARD DEVIATION[a] OF THE CARBON AND HYDROGEN DETERMINATIONS ON SUCROSE AND SOLID WASTES

Type of Sample	Number of Samples	Carbon		Hydrogen	
		Duplicates	Triplicates	Duplicates	Triplicates
Sucrose[b]	2	____	0.17	____	0.15
Sucrose[c]	2	____	0.15	____	0.19
Compost	26	____	0.29	____	0.10
Compost	56	0.22	____	0.14	____
Raw Garbage	17	0.18	0.19	0.19	0.18
Residue (Fines)	16	0.04	0.06	0.04	0.03
Residue (Organics)	8	0.21	0.23	0.22	0.18
Fly Ash	9	0.04	0.08	0.06	0.04

[a]Calculated on a pool basis for solid wastes samples

[b]National Bureau of Standards Grade.

[c]American Chemical Society Grade.

TABLE 5

EFFECT OF SAMPLE PREPARATION TECHNIQUES UPON CARBON-HYDROGEN ANALYSES

Type of Preparation	CARBON			HYDROGEN		
	Individual Percent Conc.	Average Percent Conc.	Corrected[a] Avg. Percent	Individual Percent Conc.	Average PercentConc.	Corrected[b] Avg. Percent
normal procedure for residue (fines)	29.18 30.16 27.83	29.06	—	2.22 2.69 2.29	2.40	—
fluffy fraction (17.2%[c]) residue (fines) ground in Wiley Mill using 1mm sieve	37.10 36.63 37.52	37.08	6.38	3.56 3.36 3.50	3.47	0.60
heavy fraction (81.4%) of residue (fines)pulverized in Ilver Pulverizer, passed through #60 sieve	18.90 18.90 18.97	18.89	15.38	1.17 1.20 1.43	1.27	1.03
remaining fraction (1.4%) could not be ground or pulverized or passed through #60 sieve	29.69 27.36 28.41	28.49	0.40 total 22.16	3.01 2.87 2.64	2.84	0.04 total 1.67

[a]Corrected, using the percent fraction values, to correlate average carbon value of fraction to original residue (fines) sample.

[b]Ibid, for hydrogen.

[c]All percents are on a dry basis.

B. Cost.

The cost of performing the newly developed carbon-hydrogen method was estimated assuming that: (1) the life expectancy of the glassware and heating elements is five years and of the furnace is ten years; (2) continuous operating conditions (8-hr. day, 40-hr. week, 8 holidays per year); (3) combustion tube will need repacking once every six months; (4) duplicate analyses of each sample; and (5) cost of sample preparation not included.

On a yearly basis the minimum cost of the apparatus and chemicals needed for this method is $606.00; the approximate number of analyses which can be performed is 1500 (or 750 samples); the number of man hours required is approximately 1560 hours.

The performance of this method requires only periodic attention by the analyst. Analyzing, at best, six samples a day, the analyst will have approximately two hours of free time. The cost of the labor for this method can only be expressed as man hours needed, since the salaries of analysts vary too greatly.

Since the combustion tube requires a conditioning period before a sample can be analyzed, the cost of this method is greatly reduced by continuous operation. With a conditioned combustion tube, 14 similar samples can be analyzed in duplicate before reconditioning is needed. Any number of similar samples less than 14 will require the same amount of time for preparation of the train.

The cost of the chemicals needed for each combustion tube packing is $64.79. Since the cost of lead chromate and lead dioxide is $50.40

per tube packing, a study of purification schemes for cheaper grades was performed. The lead chromates cost was greatly reduced from $18.50 to $0.90 per 100g by purchasing powder grade and preparing it for use. However, the method required to convert cheaper lead dioxide into usable material was found difficult and impractical.

In summary, this newly developed carbon-hydrogen method if employed in a continuous operation, is not expensive for the equipment and chemicals needed. The initial cost of the special built furnace is $1000; however, each additional furnace will cost $850. The major cost of this method is the labor required to perform the test. As yet, no quicker method has been developed which will give satisfactory precision with solid waste materials.

C. Sample Preparation Procedures

All incinerator effluent samples employed in the development of this method were collected by personnel in Technical Assistance Branch Division of Technical Operations, Bureau of Solid Waste Management as part of their evaluation of incinerators studies. These samples were prepared for analyses by the personnel of the Analytical Task Group, now part of Research Services Laboratory.

The laboratory personnel received the incinerator residue samples in triple plastic bags, one inside the other. Residue samples were manually separated, requiring the visual judgement of the separator, into "organics", fines", and the discarded "glass-ceramic-metal" portions. (The terminology used for these portions is defined in Table 3).

The "organics" portion is dried at 70 C to a constant weight, then ground in the Wiley Mill with the 2mm sieve attached. The "fines" portion is dried at 105 C to a constant weight, then pulverized in the Iler Pulverizer until the sample passes through a #60 sieve. The "glass-ceramic-metal" portion is weighed before being discarded.

With the Atlanta, Georgia, Incinerator Study in December 1968 even greater care has been exercised during sample preparation. Now all residue "fines" samples are further separated. With the aid of a magnet and a one-fourth inch sieve, more glass, ceramic,and metal materials can be removed before pulverizing the samples. During the pulverization step, a #20 sieve is employed to detect and remove any more unwanted materials.

Incinerator fly ash samples are prepared for analyses in the same manner as residue "fines" samples; but, since they contain very little glass, ceramic,or metal materials, fly ash samples were easy to prepare for analyses.

Raw refuse from incinerators was prepared as the residue "organics" samples. However, these samples were delivered in plastic bags to the laboratory as bulky samples which must first be put through a W-W hammermill to reduce the particle size. Even before these samples can be put into the hammermill, all noticeable glass, ceramic, and metal materials must be removed.

Almost all compost samples originated at the PHS-TVA Compost Plant, Johnson City, Tennessee and, except for a few samples prepared by the author, were prepared for analyses by the personnel at the plant site. These compost samples were shipped to the Research Services Laboratory in sealed plastic bags.

Compost samples were prepared for analyses by drying the samples in an oven, usually forced air, at 70 C to a constant weight, normally overnight. These samples were ground using a Wiley Mill with a 1mm sieve attached and stored in a tight, screw top container until the analyses. As previously mentioned, (in SectionIII. Results) all samples were redried within a few days of the analyses.

All samples were tumbled for complete mixing before analyses. In the development of this method, every samples was mixed with a spatula before a portion was removed for the analyses.